

Volume 4: Potential Ground and Surface Water Impacts

Chapter 4: Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths

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4. Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths

4.1. Introduction

The possibility of subsurface releases of gasoline from leaking underground fuel tanks (LUFTs) and piping, along with potential surface spills during tank filling and other activities, creates scenarios for hydrocarbon plume formation in groundwater downgradient from the source (See Rice *et al.*, 1999, Vol 4, Chapter 1 of this report). Fuel hydrocarbon plumes that are *not* characterized by the presence of ethanol have been studied extensively (for example, Rice *et al.*, 1995; Mace *et al.*, 1997). However, the potential role of ethanol in influencing the behavior of benzene, toluene, ethyl benzene, and xylene (BTEX) component plumes needs to be addressed because:

- A binary water-ethanol mixture can produce a cosolvency effect that serves to enhance the solubility of nonpolar organic compounds, such as BTEX constituents (see Powers and Heermann, 1999, Vol 4, Chapter 2 of this report), and
- The rapid biotransformation of ethanol can reduce the biotransformation rates of BTEX constituents, most notably benzene, by reducing the availability of electron-acceptor species (for example, dissolved oxygen and nitrate) that participate in biogeochemical oxidation reactions (see Alvarez and Hunt, 1999, Vol 4, Chapter 3 of this report).

The result of both effects, in theory, may be longer BTEX plume lengths, principally those of benzene, the constituent of greatest environmental concern.

The most direct means of measuring the effects of ethanol on benzene plume lengths is to measure benzene concentrations at LUFT sites where ethanol has been used as a gasoline additive and compare those, using appropriate statistical methods, to benzene concentrations from LUFT sites where ethanol was not in use. Unfortunately, aside from anecdotal accounts from experimental studies (for example, Hubbard *et al.*, 1994), a sufficient database of plumes from gasohol release sites does not yet exist for such an analysis.

In the absence of field data, we can employ screening-level mathematical modeling to explore plausible plume behavior scenarios. In this present evaluation, we have chosen to generate synthetic populations of benzene plumes, both with and without ethanol as a cosolute, using a physically-based, semi-analytical model with distributions of model input parameters that represent the ranges of conditions encountered in shallow aquifer settings. Model output consisted of concentrations of benzene, ethanol, and the implied biochemical oxygen demand (BOD) induced by biotransformation of ethanol for random combinations of input variables.

4.2. Methodology

4.2.1. Overview

The plume model is based upon the solution presented by Baetsle (1969) for an instantaneous, solute point-source in an infinite, homogeneous, three-dimensional (3-D) domain with uniform groundwater flow, dispersivity tensor, and biotransformation rate (modeled by first-order kinetics). Numerical integration of the source term in both space and time allows for the simulation of a finite-sized source (for example, a lens of light nonaqueous phase liquid (LNAPL) floating on the water table) and a finite release with respect to time (that is, a continuous source as opposed to an instantaneous one). Although such a semi-analytical solution is highly idealized (neglecting, for example, heterogeneities in the flow domain), it does provide a useful average model of plume behavior that can be used, in conjunction with a Monte Carlo simulation strategy, to produce probability distributions of concentrations as well as a means for assessing model sensitivity to input parameters.

One reason for utilizing probabilistic approaches in evaluating the mathematical transport model stems from the lack of sufficient field data on site-specific features of plume behavior. Probabilistic modeling of contaminant transport involves employing user-specified probability distributions of physical and chemical model variables, based on available data, to produce forecasts through multiple Monte Carlo realizations. Monte Carlo analyses are routinely used in engineering probability forecasting applications (for example, Ang and Tang [1984]). Woodbury *et al.* (1995) applied Monte Carlo analyses to practical groundwater engineering problems. In this report, the Monte Carlo approach permits uncertainties in hydrogeological data (the groundwater velocity, for example), the nature of the source, and chemical data (biotransformation rates, for example) to be translated into uncertainties regarding contaminant concentrations as a function of time and space. Parameter sensitivities can be evaluated by performing regression analyses of model output values against those of input variables.

The conceptual model for the gasohol release is a source, such as a LUFT, continually discharging a small flux of LNAPL (less than 3 gal/day), which spreads along the water table, maintaining a square footprint and a fixed thickness-to-length ratio (Figure 4-1). This corresponds to a “slow drip” scenario representative of a chronic, undetected LUFT condition and is the most likely release scenario to be encountered. The “slow drip” release scenario is in contrast to a catastrophic release scenario, which would include different source dynamics but which would, presumably, be subject to an immediate detection and remediation response.

Ethanol is assumed to be present at either a 10% volume fraction in the gasohol (for half of the realizations) or else is absent. Because of its high affinity for water, the ethanol, when present, is assumed to leach completely and instantaneously across a specified portion of the LNAPL/groundwater interface into the water (that is, all of the ethanol contained within the source flux is assumed to be injected into the aquifer along a specified portion of the interface). The ethanol migrates through the aquifer, carried along by advection as well as longitudinal, transverse, and vertical dispersion. Benzene enters the aquifer by diffusion and vertical dispersion across the LNAPL/groundwater interface, with its limited solubility, in principle, a function of the ethanol concentration at the interface.

In theory, biotransformation of the ethanol produces an anaerobic zone that, in turn, will presumably affect the biotransformation rate of benzene on a local scale (Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report). However, there is a paucity of biotransformation rates for benzene under the most anaerobic conditions (that is, sulfate-reducing and methanogenic). Moreover, although the presence of ethanol may pose significant issues, such as competitive substrate utilization and shifts in the nature of the local microbial population, there is an absence of biotransformation rate data that can be readily adapted for modeling purposes. Given the current state of knowledge, it is problematic to justify or construct a mathematical model (analytical or numerical) that specifically addresses spatial dependencies of the benzene biotransformation rate on the extent of the anaerobic shadow. At the screening level addressed by our model, therefore, we have chosen to use a global average biotransformation rate for benzene—a rate that is inversely correlated with the BOD signature in the vicinity of the source area. In other words, we assumed that, in the lognormal distribution of biotransformation rates, the slowest globally averaged rates are associated with a high BOD near the source area; whereas the highest rates occur in realizations where the ethanol-induced BOD values are comparatively low. This is a very conservative assumption because it neglects the replenishment of electron acceptors from other sources, such as diffusion of atmospheric oxygen from the vadose zone across the water table and from dissolution of ferrous and manganese-bearing oxyhydroxide minerals in the sediments. The assumption is also additionally conservative in that ethanol biotransformation effects are the *only* presumed influence on benzene biotransformation rates, thus leading to a very high inverse correlation between benzene plume lengths and BOD in the source area.

The present study uses a conservative assumption and neglects retardation as a result of adsorption. This is because (1) the Baetsle (1969) model does not directly address retardation, and (2) the superposition calculations used to quantify BOD are not valid when retardation of the substrate (ethanol) is significant. Because the organic carbon partitioning coefficients of benzene and ethanol are low, retardation resulting from adsorption would not be expected to play a large role in influencing the fate of the plumes in comparison to the influence of biotransformations. Furthermore, because the purpose of our screening model exercise is to compare benzene plume lengths between ethanol and no-ethanol scenarios, and because ethanol is not likely to exert significant effects on benzene adsorption away from the source area, the omission of retardation is not likely to exert a significant effect on the findings.

As an additional analysis, prior to calculating the Monte Carlo realizations, a sensitivity analysis was performed to assess whether the mass transfer of ethanol into groundwater would best be modeled as a point source or be distributed over all or some finite fraction of the gasoline lens. Because of its hydrophyllic nature, ethanol may not spread laterally to the same extent as the gasoline but may instead partition into the groundwater over some smaller area near the source of the leak. These analyses considered only ethanol and assumed that ethanol would biotransform based on a conservative first-order constant of 0.01 day^{-1} . It was expected that the point-source approach would lead to a localized increase in the cosolvency effect because concentrations will be greater. However, the increased cosolvency effect presumably would occur over a much smaller area, and the differences between the two modeling approaches may be insignificant.

4.2.2. Model Construction

MathCad (Mathsoft, Inc.) was used as the computational engine for the model. Parameter definitions, the complete set of governing equations, and internal model documentation are shown in Appendix A. We conducted a total of 50 Monte Carlo realizations¹ for each of two different benzene biotransformation scenarios that are described below. The probability distributions and modeling constants associated with the variable input parameters are presented in Tables 4-1a and 4-1b, respectively. For each realization, the model steps may summarized as follows:

1. The footprint of the LNAPL is calculated as a function of time based on the LNAPL flux, the porosity, the fixed LNAPL thickness-to-length ratio, and the ethanol content.
2. The ethanol plume is modeled via a prescribed flux boundary condition, where the injection of ethanol (the product of the LNAPL flux rate and the ethanol volume fraction in the LNAPL) is divided across the full spatial extent of the LNAPL.
3. BOD is calculated by superposition where, at any location and time, the BOD is indicated by the difference between the hypothetical ethanol degradation if ethanol was a conservative species (that is, a biotransformation rate of zero) minus the concentration predicted with a finite biotransformation rate, adjusted for mineralization reaction stoichiometry.
4. The source term for the benzene plume is modeled by a prescribed boundary condition, with the benzene boundary concentration (that is, its effective solubility) determined by the average ethanol concentration under the LNAPL, according to a relationship developed by Heermann and Powers (1998). The benzene flux across the prescribed concentration boundary is modeled using a relationship suggested by Johnson and Pankow (1992). The Johnson and Pankow (1992) model is for a steady-state plume; we assumed, therefore, that the benzene plume in the vicinity of the source jumps from steady-state to new steady-state as time advances. In practice, this simplifying assumption is reasonable, given that simulated plumes stabilize fairly quickly, particularly near the source, when a finite transformation rate is employed.

It is important to note that all concentrations are measured with respect to a specific depth (for example, 5 ft below the water table), owing to the three-dimensional nature of the model. In reality, groundwater samples always reflect an average across a finite depth interval because of the finite length of wells screens and sampling techniques that require some form of purging. In comparison to real water samples collected from wells with large screened intervals, model results are likely to be conservative because they do not account for sample dilution resulting from the inevitable mixing with nearby less contaminated water.

An initial set of realizations was simulated assuming no relationship between the benzene biotransformation rates and any other modeled variables (that is, the “uncorrelated” scenario). However, because the BOD values were recorded for each realization, we developed a second set of simulations, which employed the identical input parameter set except that the benzene

¹ The complexity of the calculations involved in the semi-analytic model, as shown in Appendix A, resulted in relatively slow computational execution times, so that only a small number of realizations could be run easily.

biotransformation rates were now inversely correlated with the BOD values 50 ft from the center of the LNAPL footprint (that is, the “correlated” scenario).

4.3. Results and Discussion

4.3.1. Uncorrelated Biotransformation Rates

A comparison of probability distributions of benzene concentration at 50 ft downgradient of the source location (that is, the center of the LNAPL footprint) between the scenarios with and without ethanol suggests that the cosolvency effect of ethanol is negligible, at least according to the model used in this study (Figure 4-2). This finding arises because the aqueous ethanol concentrations remain well below the volume percent-level concentrations needed to produce a cosolvency effect as a result of dilution by flowing groundwater and dispersion along the LNAPL/groundwater interface.

Additional sensitivity analyses pertaining to the ethanol source-term distribution showed that cosolvency effects are negligible whether the ethanol is added at a point source or distributed over the entire footprint of the gasoline pool. For example, it was found that when ethanol solubilized into the groundwater at 0.3 gal/day at a point, the maximum ethanol concentrations would be expected to range between 10,000 mg/L and 50,000 mg/L. In this range of aqueous ethanol concentrations, benzene solubilities would be expected to increase between 5% and 30% as a result of cosolvency (Heermann and Powers, 1998). However these increases occur over an area less than 2 m² and comprise a small fraction of the gasoline pool. When the 0.3 gal/day of ethanol was distributed over a finite area of 25 m² or greater, ethanol concentrations in groundwater were found to be less than 5000 mg/L. Below this ethanol concentration, increases in benzene solubilities are less than 3%.

The absence of any significant cosolvency effect is attributed to the slow rate of ethanol mass transfer from the gasoline into the groundwater system. Cosolvency effects are more likely to be encountered following a catastrophic release of gasoline where large volumes of ethanol may move rapidly into the groundwater. However, even under this scenario, cosolvency effects are expected to be small. For example, model simulations by Heermann and Powers (1998) showed that the length of a BTEX plume would increase by only about 10% due to presence of ethanol in the gasoline. Despite the absence of cosolvency, the net volume of ethanol and BTEX solubilizing in groundwater may be much greater for the slow-leak scenario considered in this analysis than with a catastrophic scenario. The slow leak may go undetected for long periods of time whereby a catastrophic release would probably be detected much more rapidly.

4.3.2. Correlated Biotransformation Rates

Unlike the uncorrelated scenario, which neglects the effects of ethanol on benzene biotransformation rates, the correlated scenario indicates an observable difference in benzene concentration distributions near the source area between the ethanol and no-ethanol realizations (Figure 4-3). The significance of the biotransformation effect is also evident in comparing the influence of the LNAPL flux terms (Figure 4-4). When biotransformation rates are uncorrelated with the BOD, there is little forecast dependence of benzene concentrations on the flux term because of the limited solubility of benzene in water. Any relationship at all would be a result of

the expanded size of the LNAPL/groundwater interface. On the other hand, in the correlated scenario, benzene concentrations are significantly influenced by the LNAPL flux, primarily because larger quantities of ethanol in the source term imply larger BOD values and, hence, lower benzene biotransformation rates.

This biotransformation effect on benzene concentrations appears to diminish with distance downgradient from the source because of changes in parameter sensitivity. For example, near the source area (for example, 50 ft downgradient from the LNAPL center), benzene concentrations exhibit a relatively weak dependence on groundwater velocity, but they are instead somewhat differentiated, based on whether or not ethanol is present as a cosolute (Figure 4-5). Nevertheless, the linear regression analyses we performed on the relationships between concentration and input variable (by rank) as a function of distance suggest that variability in groundwater velocity becomes the dominant influence on variability in concentration forecast downgradient from the source (Figure 4-6). This is at the expense of the biotransformation rate influence, which, in turn, declines significantly away from the source area.

Interpreted median plume lengths, defined by the distance from the LNAPL center to the 1- and 10-parts-per-billion (ppb) concentration contours, are provided in Table 4-2 for the results of this study as well as two other recent studies (Malcolm Pirnie, Inc., 1998; Ulrich, 1999). The agreement between the models is good, suggesting a modest potential for an extension of benzene plume lengths, less than a factor of two, in the presence of ethanol over cases where ethanol is not used. It is important to stress, however, that this finding is very preliminary in the absence of the data needed for more refined estimates. Moreover, it is particularly important to stress the conservative nature of the model assumptions, notably the global reduction in benzene biotransformation rates associated with the ethanol-induced BOD, and the non-depth-averaged benzene concentration predictions. Thus, the model results should be viewed as representing an expected upper bound to the effects under consideration.

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Figures

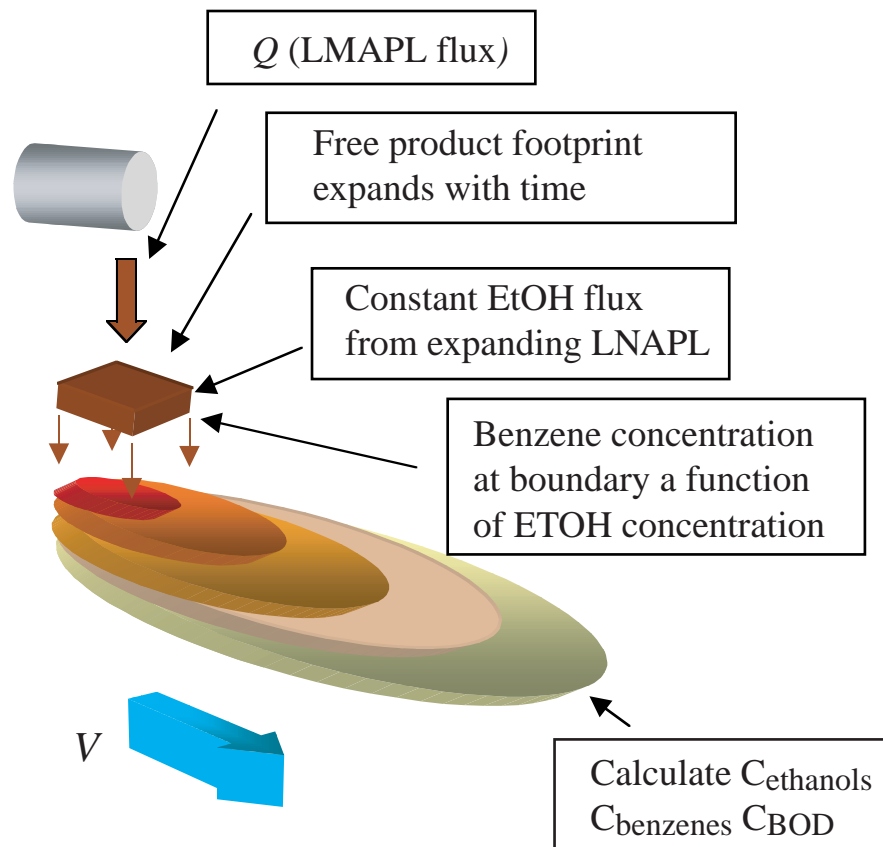


Figure 4-1. Idealized model of LNAPL gasohol release to the subsurface.

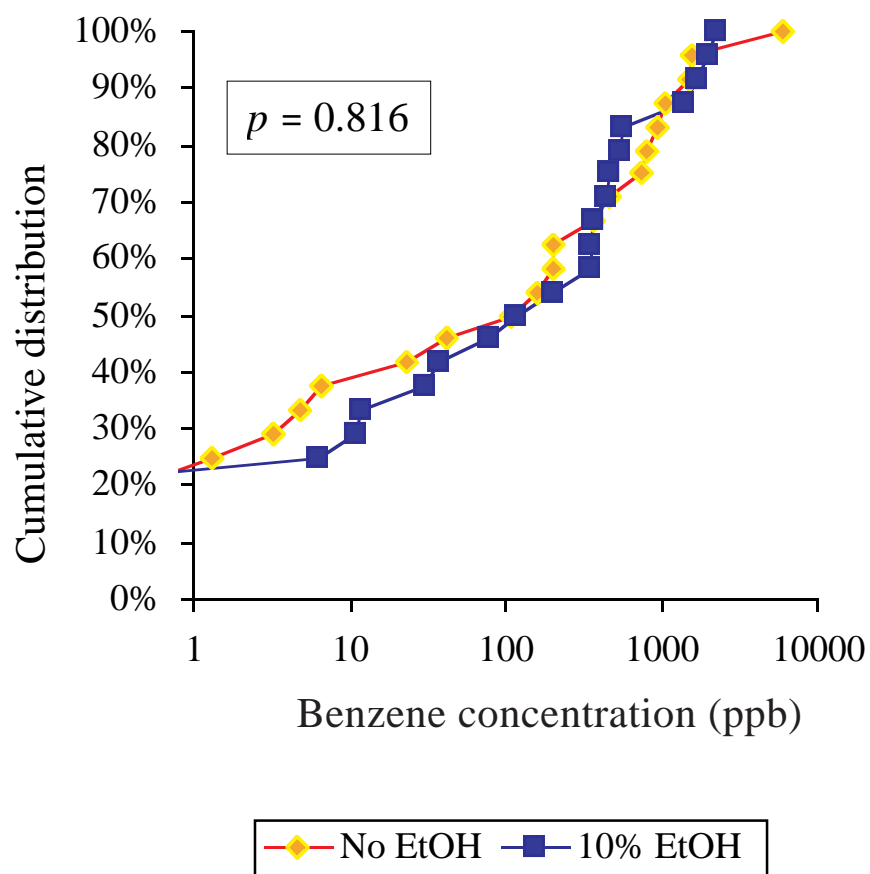


Figure 4-2. Forecast probability distributions of benzene concentrations 50 ft downgradient from the center of the LNAPL footprint. A comparison between gasolines with and without ethanol when benzene biotransformation rates are uncorrelated with biochemical oxygen demand.

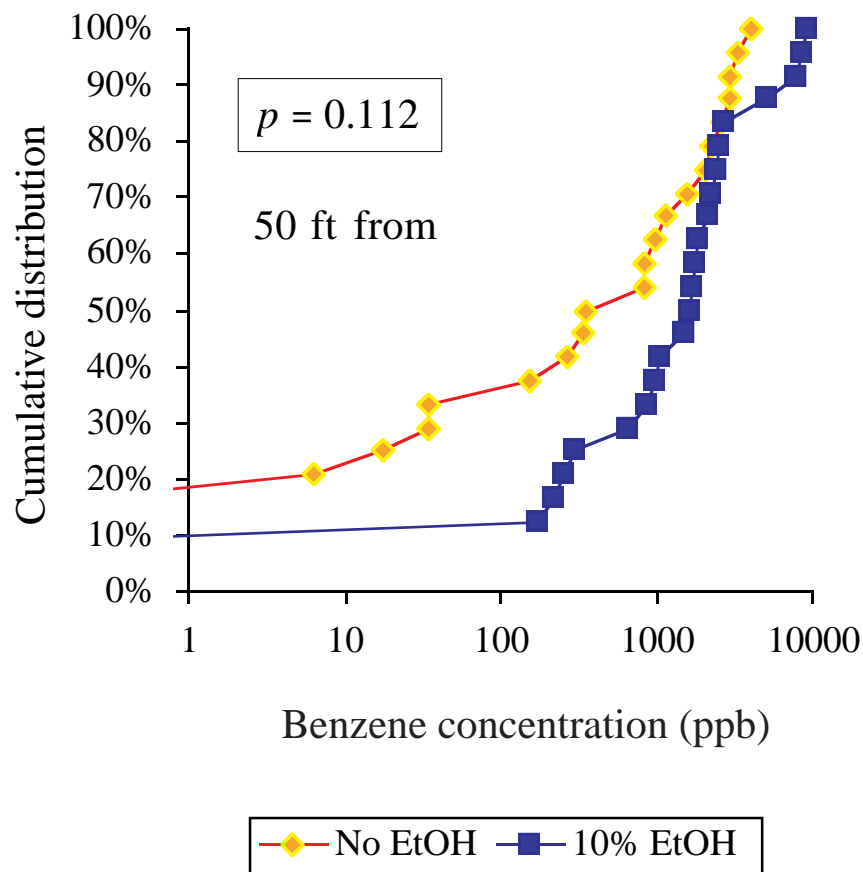


Figure 4-3. Forecast probability distributions of benzene concentrations 50 ft downgradient from the center of the LNAPL footprint. A comparison between gasolines with and without ethanol when benzene biotransformation rates are correlated with biochemical oxygen demand.

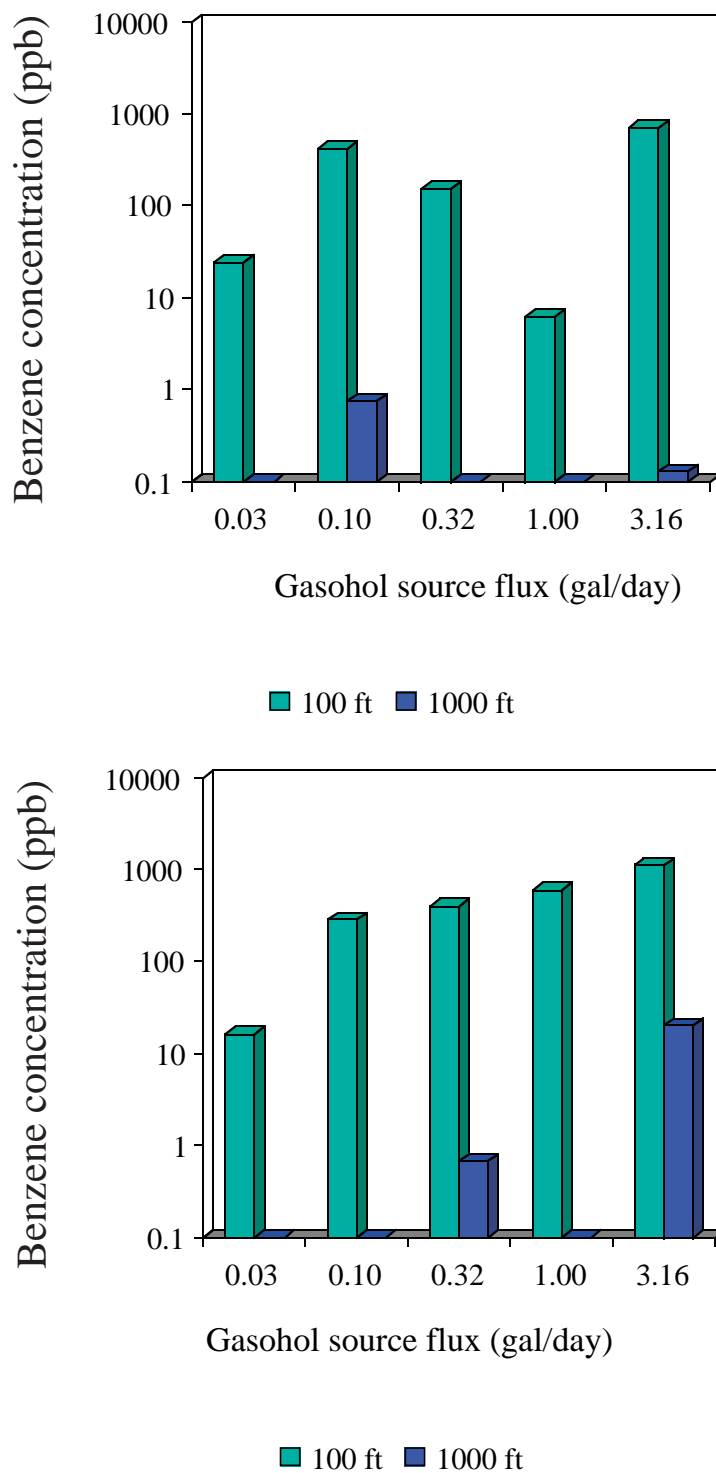


Figure 4-4. Forecast influences of LNAPL flux source term on benzene concentrations; (a) uncorrelated and (b) correlated benzene biotransformation rates.

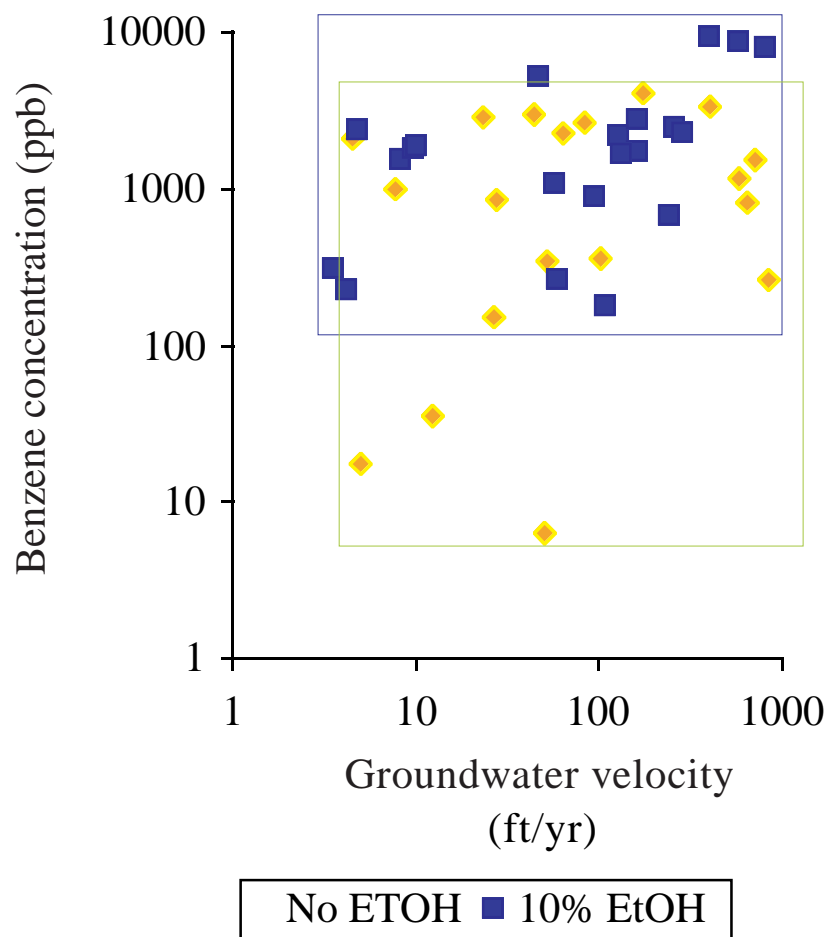


Figure 4-5. Forecast relationship between benzene concentrations 50 ft downgradient from the center of the LNAPL footprint and groundwater velocity, with and without ethanol, when benzene biotransformation rates are correlated with biochemical oxygen demand.

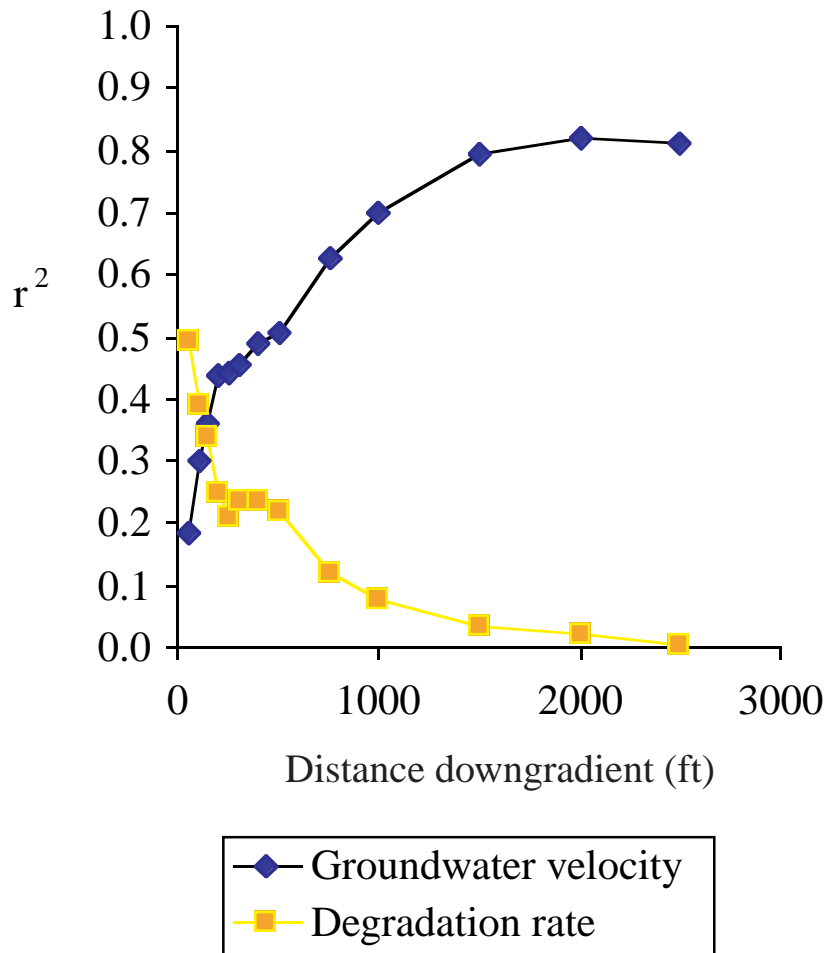


Figure 4-6. Influence of input variables on forecast benzene concentrations as a function of distance, as indicated by rank correlation (for correlated benzene biotransformation rates).

Tables

Table 4-1a. Probability distribution input parameters for modeled Monte Carlo forecasts.

Parameter	Description	Remarks	Prescribed distribution
X_{EtOH}	Ethanol fraction in gasohol	Represents maximum expected in California reformulated gasoline	1% and 10%, by mass or mole fraction
Q	Rate of NAPL replenishment	Based on current uncertainty of tank release monitoring	Loguniform distribution 3.16–0.0316 [log(uniform range of 0.5 to–1.5)]
T	NAPL lens thickness-to-length ratio	Based on estimates from Dooher, 1998	Loguniform distribution 0.1–0.01 [log(uniform range of –1 to –2)]
λ_{EtOH}	Ethanol first-order degradation rate	Estimated from laboratory experiments of Corseuil <i>et al.</i> , 1998; Alvarez and Hunt, 1999. Howard <i>et al.</i> (1991) reports a range of half-lives 1/3 to 2/5 faster.	Lognormal distribution. 5th percentile = $1.28 \times 10^{-1} \text{ day}^{-1}$ ($t_{1/2}$ = 5.43 days) mean = $2.46 \times 10^{-1} \text{ day}^{-1}$ ($t_{1/2}$ = 2.82 days) 95th percentile = $4.51 \times 10^{-2} \text{ day}^{-1}$ ($t_{1/2}$ = 1.67 days)
λ_{Benzene}	Benzene first-order degradation rate	Rice <i>et al.</i> , 1998. Median value may be fairly typical as a macroscopic average for many sites (e.g., Ulrich, 1999; Dooher, 1998).	Lognormal distribution. 5th percentile = $9.75 \times 10^{-5} \text{ day}^{-1}$ ($t_{1/2}$ = 7110 days or 19.5 years) mean = $3.65 \times 10^{-2} \text{ day}^{-1}$ ($t_{1/2}$ = 19 days) 95th percentile = $1.23 \times 10^{-1} \text{ day}^{-1}$ ($t_{1/2}$ = 5.6 days)
p	Fraction of NAPL footprint over which ethanol partitions in water.	Postulation based (Powers and Heermann, 1999).	Loguniform distribution 0.1– 0.01 [log(uniform range of –1 to –2)]
K	Hydraulic conductivity	Values typifying California hydrogeology (Dooher, 1998). Values supported by Mackay <i>et al.</i> , 1985, and Guven <i>et al.</i> , 1984.	Lognormal distribution. 5th percentile = $3.82 \times 10^{-6} \text{ m/s}$ (0.33 m/day) mean = $1.25 \times 10^{-4} \text{ m/s}$ (10.8 m/day) 95th percentile = $4.75 \times 10^{-4} \text{ m/s}$ (41 m/day)
∇h	Hydraulic gradient	Values typifying California hydrogeology (Dooher, 1998). Values supported by Mackay <i>et al.</i> , 1985, and Guven <i>et al.</i> , 1984.	Lognormal distribution. 5th percentile = 1.42×10^{-3} mean = 1.66×10^{-2} 9th percentile = 5.58×10^{-2}
ϕ	Porosity	Based on 252 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998) and Jury (1985).	Normal distribution. mean = 0.42 standard deviation = 0.07

Table 4-1b. Model constants for input parameters.

Parameter	Description	Remarks	Prescribed distribution
X_{Benzene}	Benzene fraction in gasahol	Represents maximum expected in California reformulated gasoline	1.5%, by mass or mole fraction
α_x	Longitudinal dispersivity.	Based on results presented in Gelhar <i>et al.</i> (1992).	20 ft
α_y	Horizontal transverse dispersivity.	Based on results presented in Gelhar <i>et al.</i> (1992).	2 ft
α_z	Vertical transverse dispersivity.	Based on results presented in Gelhar <i>et al.</i> (1992).	0.5 ft
C_w	Benzene solubility in pure water		1780 ppm
β	Volume fraction of EtOH at the break point between the linear and the log-linear model	Powers and Heermann (1999).	0.27
C_β	Benzene solubility at β .	Powers and Heermann (1999).	4420 ppm
D_e	Effective molecular diffusion coefficient	Taken to be identical for ethanol and benzene.	$5 \times 10^{-10} \text{ m}^2/\text{s}$

Table 4-2. Summary of simulation results indicative blended gasoline plume length effects.

Study	Plume lengths: regular gasoline	Plume lengths: blended gasoline
LLNL screening model	200-250 ft at 10 ppb 200-250 ft at 1 ppb	250-300 ft at 10 ppb (~20% longer) 400-500 ft at 1 ppb (~100% longer)
Malcolm Pirnie, Inc. (1998)	145-330 ft at 1 ppb Median: 240 ft	195-420 ft at 1 (ppb) Median: 310 ft (~30% longer)
Governor's Ethanol Coalition (Ulrich, 1999) model of Borden aquifer site	200 ft	365 ft (~80% longer)
Waterloo blended methanol-gasoline field study ^a (Hubbard <i>et al.</i> , 1994)	~75 ft	~115 ft (50% longer)

^a Gasoline with 15% MeOH, introduced as a slug source in a controlled field experiment.

Appendix A

Semi-analytical Gasohol Solute Transport Model in 3-D with a Finite, Time-dependent LNAPL Source

Semi-Analytical Gasohol Solute Transport Model in 3-D with a Finite, Time-Dependent LNAPL Source

This worksheet contains a full 3-D semi-analytical model for the development of ethanol, benzene, and biochemical oxygen demand plumes emanating from a light non-aqueous phase liquid (LNAPL) source as a function of time and space. The LNAPL source itself grows over time, depending on the input of fresh gasohol. The transport model is based on spatial and temporal integration of the Baetsle (1969) instantaneous point source solution in 3-D. The ethanol source term consists of a prescribed flux boundary condition across the LNAPL/groundwater interface which changes as a function of time as the LNAPL pool grows. The benzene source term is handled by a prescribed boundary condition, with the prescribed benzene boundary concentration (that is, its effective solubility) determined by the average ethanol concentration under the LNAPL (again, a function of time). The coupling between the source terms is handled by equations provided by Johnson and Pankow (1992) and Heerman and Powers (1998). The biochemical oxygen demand is calculated by superposition with respect to the ethanol plume.

**Unit definitions and
MathCad parameters ...**

$$\text{ppb} := 10^{-6} \frac{\text{gm}}{\text{L}}$$

$$\text{ppm} := 10^{-3} \frac{\text{gm}}{\text{L}}$$

$$\text{TOL} \equiv 1 \cdot 10^{-4}$$

$$\text{ORIGIN} \equiv 1$$

Aquifer properties (for downgradient plume simulation)

Hydraulic conductivity: $K := 10 \frac{\text{ft}}{\text{day}}$

Hydraulic gradient: $I := 0.002$

Porosity: $\phi := 0.25$

Pore velocity by Darcy's law: $v := \frac{K \cdot I}{\phi}$ $v = 29.219 \frac{\text{ft}}{\text{yr}}$

Dispersion tensor:

Longitudinal: $\alpha_x := 20 \text{ ft}$ $D_x := \alpha_x \cdot v$

Transverse: $\alpha_y := 2 \text{ ft}$ $D_y := \alpha_y \cdot v$

Vertical: $\alpha_z := 0.5 \text{ ft}$ $D_z := \alpha_z \cdot v$

Gasohol source properties

NAPL replenishment rate:

$$Q := 0.5 \frac{\text{gal}}{\text{day}}$$

Ethanol mass/mole/volume fraction in gasohol:

$$X_{\text{EtOH}} := 10 \%$$

Benzene mass/mole/volume fraction in gasohol:

$$X_{\text{B}} := 1.5 \%$$

NAPL thickness-to-length ratio:

$$T_{\text{ratio}} := 0.1$$

Solute properties

First-order decay coefficient for ethanol:

$$\lambda_{\text{EtOH}} := 0.01 \text{ day}^{-1}$$

First-order decay coefficient for benzene:

$$\lambda_{\text{B}} := 0.003 \text{ day}^{-1}$$

Effective molecular diffusion
coefficient (assume the same
for both ethanol and benzene):

$$D_{\text{e}} := 5 \cdot 10^{-10} \frac{\text{m}^2}{\text{sec}}$$

Governing equations for ethanol plume model

**Size of square-footprint
NAPL/groundwater
interface**

$$\varepsilon := 1 \text{ cm}$$

(Used to prevent divide-by-zero error)

$$L_p(t) := \sqrt[3]{\frac{Q \cdot t \cdot (1 - X_{\text{EtOH}})}{T_{\text{ratio}} \cdot \phi}} + \varepsilon$$

(Length of one side of the LNAPL lens as a function of time, corrected for product loss due to ethanol dissolution. LNAPL lens is assumed to have a square footprint, with a thickness to length ratio of T_{ratio} .)

**Ethanol source function,
assuming a specified flux across
the NAPL/groundwater interface**

Density of ethanol:

$$\rho_{\text{EtOH}} := 0.7 \frac{\text{gm}}{\text{cm}^3}$$

Implied constant ethanol mass
injection rate:

$$M_{\text{EtOH}} := Q \cdot X_{\text{EtOH}} \cdot \rho_{\text{EtOH}}$$

Fraction of NAPL footprint over
within which ethanol partitions
into water:

$$p := 25 \%$$

$$M_{f\text{EtOH}}(t) := \frac{M_{\text{EtOH}}}{p \cdot L_p(t)^2}$$

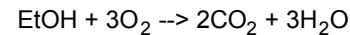
(The implied ethanol flux, based on assumption of complete, instantaneous partitioning into the water phase, is divided over the some portion, p , of the growing NAPL footprint.)

Plume model for ethanol, based on the solution of Baetsle (1969). The solute transport model used for ethanol is based upon an instantaneous point source (that is, mass slug) solution into a 3-D domain. To modify the mathematical solution for the conditions of interest, the point source is integrated over finite distances in the x - and y -directions to simulate leaching from the LNAPL lens and is integrated in time to emulate a finite source (the changing size of the LNAPL lens over time is accounted for). The source functions are multiplied by 2 for superposition of the source to account for the boundary condition imposed by the water table.

$$C_1(x, y, z, t, \lambda) := \int_0^t \left[\frac{p \cdot L_p(t - \tau)}{2} - \frac{-p \cdot L_p(t - \tau)}{2} \right] \frac{2 \cdot M_{fEtOH}(t - \tau)}{8 \cdot (\pi \cdot \tau)^{\frac{3}{2}} \cdot \sqrt{D_x \cdot D_y \cdot D_z}} \cdot \exp \left[- \left[\frac{(x - x_s)^2}{4 \cdot D_x \cdot \tau} + \frac{(y - y_s)^2}{4 \cdot D_y \cdot \tau} + \frac{z^2}{4 \cdot D_z \cdot \tau} + \lambda \cdot \tau \right] \right] dx_s dy_s d\tau$$

Biochemical oxygen demand (BOD) for mineralized of ethanol to CO_2

Reaction stoichiometry:



Molecular weights:

$$MW_{EtOH} := 46.07 \frac{\text{gm}}{\text{mol}} \quad (\text{Ethanol})$$

$$MW_{O_2} := 32 \frac{\text{gm}}{\text{mol}} \quad (O_2)$$

Biochemical oxygen demand
weighting factor:

$$w_{BOD} := 3 \cdot \frac{MW_{O_2}}{MW_{EtOH}}$$

Ethanol biotransformation shadow

$$\delta e(x, y, z, t, \lambda) := C_1(x, y, z, t, 0 \text{ day}^{-1}) - C_1(x, y, z, t, \lambda)$$

Analysis: Ethanol plume and anaerobic shadow

Elapsed time since release began

$$t := 30 \text{ yr}$$

Cumulative ethanol mass introduction over release period

$$\Sigma_{\text{EtOH}} := M_{\text{EtOH}} \cdot t$$

$$\Sigma_{\text{EtOH}} = 1.452 \cdot 10^3 \text{ kg}$$

Concentrations versus position for example parameter set

$$x := 40 \text{ ft}$$

$$y := 0 \text{ ft}$$

$$z := -5 \text{ ft}$$

Ethanol

$$C_1\{x, y, z, t, \lambda_{\text{EtOH}}\} = 3.227 \text{ ppm}$$

BOD

$$\delta e\{x, y, z, t, \lambda_{\text{EtOH}}\} \cdot w_{\text{BOD}} = 41.847 \text{ ppm}$$

$$x := 100 \text{ ft}$$

$$y := 0 \text{ ft}$$

$$z := -15 \text{ ft}$$

Ethanol

$$C_1\{x, y, z, t, \lambda_{\text{EtOH}}\} = 0.674 \text{ ppb}$$

BOD

$$\delta e\{x, y, z, t, \lambda_{\text{EtOH}}\} \cdot w_{\text{BOD}} = 13.165 \text{ ppm}$$

Governing equations for benzene plume model

Average ethanol concentration vs. time at LNAPL/water boundary. The specified concentration boundary condition for benzene (see below) requires that the ethanol concentration at the LNAPL/groundwater interface be known. Because the ethanol source function is a specified flux at the interface, this value cannot be defined precisely at the interface. As an alternative, a finite-thickness boundary layer may be delineated underneath the LNAPL where an ethanol boundary concentration may be defined. For computational simplicity, and to meet as much as possible mathematical constraints required for the Johnson and Pankow (1992) solution to hold (see below), an average ethanol concentration across the entire LNAPL/groundwater interface is calculated as a function of time. This value is then used to calculate an average benzene boundary concentration. To simplify computations, the averaged ethanol concentrations are stored in an array to avoid having to recalculate the integrals in the equation for C_1 as a function of time. This necessitates time-discretizing the continuous benzene source term, rather than assuming a continuous integral.

Assumed boundary layer thickness: $b := 1 \text{ mm}$

Ethanol density: $\rho_{\text{EtOH}} := 0.7 \frac{\text{gm}}{\text{cm}^3}$

Time discretization: $N_t := 20$ $\Delta t := \frac{t}{N_t}$ $i := 1..N_t$ $t_{d_i} := (i - 0.5) \cdot \Delta t$

Discretization of NAPL pool length as a function of time: $L_{d_i} := L_p(t_{d_i})$

Spatial discretization of NAPL/groundwater interface over time for estimating average ethanol concentration:

$N_s := 5$ $\Delta x_i := \frac{L_{d_i}}{N_s}$ $j := 1..N_s$ $x_{d_{i,j}} := \frac{-L_{d_i}}{2} + (j - 0.5) \cdot \Delta x_i$

$\Delta y_i := \frac{L_{d_i}}{N_s}$ $k := 1..N_s$ $y_{d_{i,k}} := \frac{-L_{d_i}}{2} + (k - 0.5) \cdot \Delta y_i$

Temporal discretization of average ethanol concentration:

$$f_i := \frac{\sum_j \sum_k C_i \left\{ x_{d_{i,j}}, y_{d_{i,k}}, \frac{-b}{2}, t_{d_i}, \lambda_{\text{EtOH}} \right\}}{N_s^2 \cdot \rho_{\text{EtOH}}}$$

(Average volume fraction of ethanol under the LNAPL pool in ethanol-water mixture over each discrete time interval.)

Average benzene concentration and benzene mass flux/area vs. time at the LNAPL/groundwater boundary. Because of the limited solubility of benzene in water, the benzene source term is one of a prescribed concentration boundary, as opposed to the prescribed flux boundary condition used for ethanol. Because the cosolvency effect of ethanol can increase the solubility of benzene, the boundary condition solubility of benzene is calculated from the mean ethanol concentration under the LNAPL pool as a function of time and the method proposed by Heerman and Powers (1998). The mass flux of benzene per unit area is calculated using the solution of Johnson and Pankow (1992). Their solution is one for a steady-state plume that has developed beneath a LNAPL pool. In this model, it is assumed that the system jumps from steady-state to steady-state over each discrete time interval. The mass flux is then updated accordingly.

Pure benzene solubility in pure water:

$$C_w := 1780 \text{ ppm}$$

Volume fraction of ethanol in the aqueous phase at the break point between the linear and log-linear models:

$$\beta := 0.27$$

Solubility of benzene at β :

$$C_\beta := 4420 \text{ ppm}$$

Equilibrium concentration of benzene in the binary mixture (for $f < \beta$) after Heerman and Powers (1998):

$$C_{B_i} := \left\{ 1 - \frac{f_i}{\beta} \right\} \cdot C_w \cdot X_B + \frac{f_i}{\beta} \cdot C_\beta \cdot X_B$$

Benzene mass flux/area over discrete time intervals, after Johnson and Pankow (1992):

$$M_{fB_i} := C_{B_i} \cdot \phi \cdot \sqrt{\frac{4 \cdot (D_z + D_e) \cdot v}{\pi \cdot L_{d_i}}}$$

Plume model for benzene, based on the solution of Baetsle (1969). The form of this mathematical solution for the benzene plume is similar to that for ethanol, except that the source term has been discretized over a specified finite number of time intervals. The equation has been split into two terms here simply for clarity.

$$\psi(x, y, z, t, \lambda) := \frac{2}{8 \cdot (\pi \cdot t)^{\frac{3}{2}} \cdot \sqrt{D_x \cdot D_y \cdot D_z}} \cdot \exp \left[\frac{-(x - v \cdot t)^2}{4 \cdot D_x \cdot t} - \frac{y^2}{4 \cdot D_y \cdot t} - \frac{z^2}{4 \cdot D_z \cdot t} - \lambda \cdot t \right]$$

$$C_2(x, y, z, t, \lambda) := \sum_i \int_{t_{d_i} - \frac{\Delta t}{2}}^{t_{d_i} + \frac{\Delta t}{2}} \int_{-\frac{L_{d_i}}{2}}^{\frac{L_{d_i}}{2}} \int_{-\frac{L_{d_i}}{2}}^{\frac{L_{d_i}}{2}} M_{fB_1} \cdot \psi \{x - x_s, y - y_s, z, t - \tau, \lambda\} dx_s dy_s d\tau$$

Concentrations versus position for example parameter set

$x := 40 \text{ ft}$ $y := 0 \text{ ft}$ $z := -5 \text{ ft}$

Benzene $C_2(x, y, z, t, \lambda_B) = 399.296 \text{ ppb}$

$x := 100 \text{ ft}$ $y := 0 \text{ ft}$ $z := -15 \text{ ft}$

Benzene $C_2(x, y, z, t, \lambda_B) = 10.457 \text{ ppb}$

References

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